

Study on Thermal Relaxation in Metallic Glasses¹

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ABSTRACT

Differential scanning calorimetry (DSC) measurements were carried out for a bulk metallic glass (BMG), $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10.0}\text{Be}_{22.5}$ (Johnson alloy), below and above the glass transition temperature T_g . Apparent values of T_g were determined from the DSC curves. A wide range of heating rate, $q = dT/dt = 0.1\text{--}100$ K/min, was adopted for the experiment, and the q dependence of T_g was investigated. The T_g value nonlinearly decreased with decreasing q , the rate of decrease gradually diminished, and T_g approached a constant value at low q . The data were analyzed by a T_g vs $\log q$ formula composed of static and kinetic terms. The first term was a constant, while the second one arose from a hopping type relaxation $\tau \propto \exp(E/RT)$. The activation energy E was determined, and the value was compared with those obtained by analyzing existing data for other kind of BMG.

KEY WORDS: bulk metallic glasses; differential scanning calorimetry;

glass transition temperature; heating-rate dependence; hopping type relaxation; Johnson alloy.

1. INTRODUCTION

In amorphous or glassy materials, a variety of relaxation phenomena are observed in various physical properties at various temperatures. We are interested in mechanical and thermal relaxations near glass transition temperature T_g . Shear viscosity, which is proportional to a mechanical relaxation time, has been studied for inorganic [1,2] and organic [2] glasses near T_g . The phenomenon called the stabilization process showing an unstable metastable relaxation has been studied below and near T_g by measuring a time dependence of specific heat [3-5].

In the present study, the differential scanning calorimetry (DSC) measurements are carried out for studying the heating-rate dependence of T_g . It seems to be a common agreement of glass scientists that the glass transition is closely related to a relaxation phenomenon. The most strong evidence of this is that the glass transition temperature apparently depends on the heating rate. The phenomenon is, however, not so thoroughly investigated, and this is the motivation of our study.

There are a variety of glass-formers with different composing elements, and glasses are conveniently divided into inorganic, organic, and metallic glasses. For realizing the glassy state, a sufficiently rapid cooling is sometimes needed. Especially in the case of usual metallic glasses, very severe quenching processes are necessary, and only thin film glass specimens can be obtained. However, it has been found that metallic glasses with large sizes can be formed through rather mild cooling process for some kinds of complex alloy systems, and these are called bulk metallic glasses (BMG). A great deal of scientific and technological interests are recently focused to BMG, and there still remain many problems to be solved for understanding characteristics of such glasses. In the present study, a kind of BMG is adopted for the specimen to be investigated.

2. MEASUREMENTS

2.1 Specimens

The usual BMG's extensively studied are ternary alloys such as Pd-Ni-P and La-Al-Ni. More complex alloys are recently noted because of their excellent properties. Among these, $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ called the Johnson alloy (JA) is attractive due to its high glass-forming ability. This alloy can be cast into bulk glassy rods with thicknesses ranging between 5 cm and 10 cm [6], and its possible practical uses are especially expected. We adopted the JA glass as our specimen to be studied.

2.2 Procedure

Thermometric measurements were carried out using a DSC apparatus DSC8230 (Rigaku Co., Ltd, Tokyo, Japan). The measurable temperature range is $-150^{\circ}\text{C} - 725^{\circ}\text{C}$; the DSC range is $100\text{ }\mu\text{W} - 100\text{ mW/FS}$; the maximum heating rate is

150°C/min; the maximum specimen volume is 100 µl. The DSC data are digitally recorded and displayed on a chart. In the present measurements, about 10 mg of specimen enclosed in an air-tight Al pan is used. Usually a constant Ar gas flow is applied through the specimen chamber. The DSC measurements were performed in a temperature range below and above the glass transition temperature T_g . A wide range of the heating rate, $q=dT/dt=0.1 - 100$ K/min, was adopted for the experiment, and long time scale (small q) measurements were especially regarded to be important. The DSC curves for various heating rate q are shown in Fig. 1. The apparent value of T_g was obtained in a conventional manner. Namely, the background part at low temperatures and the rapid rise part near T_g were extrapolated, and T_g was determined as the intercept of the two extrapolations.

3. RESULTS AND ANALYSIS

The observed values of glass transition temperature T_g (K) are plotted against the heating rate q (K/min) in Fig. 2. The T_g value decreases with decreasing q , and the change is nonlinear. The rate of decrease gradually diminishes, and the T_g seems to approach a constant value at low q .

The data are analyzed using the formula derived by the authors, and the procedure of the derivation is as follows. When the temperature of a glass is increased with a constant heating rate $q=dT/dt$, a relaxation is considered to occur near the apparent T_g within a time interval Δt in a temperature range ΔT . Let the relaxation time be τ , and $\tau q = \tau (\Delta T / \Delta t)$. Now an approximation $\tau \sim \Delta t$ is adopted, and then

$$\tau q = \Delta T.$$

We postulate the hopping type relaxation time $\tau = \tau_0 \exp (E / RT)$, and here τ_0 is the pre-exponential factor, E is the activation energy, and R is the gas constant. We assume that $E \sim \text{constant}$ since the temperature range we are considering is not so wide. Another approximation $T \sim T_g$ can also be used. Namely,

$$[\tau_0 \exp (E / RT_g)] = \Delta T.$$

From this relation, the following formula can be obtained.

$$T_g = C_1 [\log (C_2 / q)]^{-1}; \quad C_1 = ME/R, \quad C_2 = \Delta T / \tau_0,$$

where $M=1/\ln 10=0.434$, and \log and \ln mean the common and natural logarithms. The above formula can be transformed to a more convenient form as

$$T_g = [A - B \log q]^{-1}; \quad A = (\log C_2) / C_1, \quad B = C_1^{-1}$$

Furthermore, we add a constant to the right hand side of the above formula, and finally obtain the expression

$$\begin{aligned} T_g &= T_{g0} + [A - B \log q]^{-1}; \\ A &= (R / ME) \log (\Delta T / \tau_0), \quad B = R / ME. \end{aligned} \quad (1)$$

The temperature width ΔT can depend on T_g , but not so greatly. Thus A is approximately regarded as a constant. Note that the formula for T_g is composed of two terms. The second term represents the contribution of the relaxation near T_g ("kinetic term"), and the first term corresponds to the value of T_g for $q \rightarrow 0$ ("static term"). The physical meaning of static term is discussed in the next section.

The data shown in Fig. 2 are fitted to Eq. (1), and the fitted curve is shown in the figure. The fitting seems to be reasonable, and obtained values of the fitting parameters

are as follows:

$$T_{g0} = 578 \text{ K}, A = 1.67 \cdot 10^{-2} \text{ K}^{-1}, B = 1.01 \cdot 10^{-2} \text{ K}^{-1}.$$

Using these values, the activation energy and the pre-exponential factor for the relaxation process can be determined, and the results are

$$E = 1.90 \text{ kJ/mol}, \log \tau_0 = -0.65,$$

and here an experimentally adequate value $\Delta T = 10 \text{ K}$ is used. The value of $\log \tau_0$ is somewhat ambiguous because of the uncertainty of ΔT , while the E value is much more reliable.

4. DISCUSSION

Now the derived formula Eq. (1) is reconsidered. First, the kinetic term (second term) is considered. In order to derive the form of the term, the hopping type relaxation time was postulated. In our study of shear viscosity of glasses [1,2], it has been found that the relaxation is of the hydrodynamic regime at higher temperatures showing the Vogel-Tammann-Fulcher (VTF) type relaxation time $\tau = \exp[\text{const}/(T - T_0)]$, $T_0 = \text{const}$, and the relation is of the hopping regime showing the relaxation time $\tau = \exp(E/RT)$ at lower temperatures. A crossover of the two relaxation types occurs at a temperature slightly above the glass transition temperature T_g . Since the present experiment of heating-rate dependence was performed in a temperature range below T_g , it was considered that the hopping type relaxation time should be adopted. Second, the static term (first term) is considered. It is well known that in glass-forming materials the entropy difference $\Delta S = S(\text{liquid}) - S(\text{crystal})$ vanishes at a definite temperature T_K called the Kauzmann temperature. It is considered that the "static" glass transition occurs at this temperature, which is also called the "ideal" glass transition temperature. The Kauzmann temperature T_K is lower than the conventional glass transition temperature $T_{gc} = T_g(q = 10 \text{ K/min})$. It was shown experimentally that the ratio $r = T_{gc}/T_K = 1.1 - 1.9$ in various glasses [7]. In our data, if $T_{g0} \sim T_K$ and then the ratio T_{g0}/T_{gc} takes a value in the above range. The evaluated ratio is $r = T_{gc} (= 619 \text{ K})/T_{g0} (= 578 \text{ K}) = 0.93$. This value is not so unreasonable, but seems to be somewhat small. When the heating-rate experiment is extended to smaller q region, then it may be possible that the experimental T_{g0} value decreases and the ratio r increases. It is noted here that a long scale (small q) heating-rate experiment offers a method for determining the Kauzmann temperature.

Results of studies by other authors concerning the heating-rate problem are cited in the following. Gutzow and Schmelzer [8] postulated the hopping type relaxation time, and derived the same form as our formula Eq. (1). The expression for the constant B which is related to the activation energy is the same, and that for the constant A is somewhat different. The authors noted that the form has been derived empirically by other investigators [9,10]. Brüning and Samwer [11] proposed a formula for fitting to their experimental data as

$$T_g = T_{g0}' + A'/\ln(B'/q), \quad (2)$$

where T_{g0}' , A' , and B' are constants. They derived the formula by an analogy to the relaxation time of Vogel-Tammann-Fulcher type. We do not know whether the idea is reasonable or not. However, we can utilize their experimental results. The form of Eq. (2) is essentially the same as that of Eq. (1). The relations between the constants

appearing in these equations are

$$T_{g0} = T_{g0}', A = (1/MA') \log B', B = (1/MA')$$

Brüning and Samwer carried out the heating-rate experiment for several metallic glasses, oxide glasses, and polymer glasses. They give the values of T_{g0}' , A' , and B' for all of these glasses. After assuming that the relaxation of hopping type is occurring in these cases, we can evaluate the activation energy values for the relaxation in these materials. Here only the cases of metallic glasses are taken into account, and the evaluated activation energy values are given in the following [(a) - (c)], together with the result for the JA glass determined by us [(d)]. The values of T_{g0} are also shown here.

(a) $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{19}\text{Si}_1$

$$T_{g0} = 518 \text{ K}, E = 4.47 \text{ kJ/mol},$$

(b) $\text{Pd}_{77.5}\text{Si}_{16.5}\text{Ag}_{6.0}$

$$T_{g0} = 576 \text{ K}, E = 6.40 \text{ kJ/mol},$$

(c) $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$

$$T_{g0} = 338 \text{ K}, E = 16.6 \text{ kJ/mol},$$

(d) $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10.0}\text{Be}_{22.5}$

$$T_{g0} = 578 \text{ K}, E = 1.90 \text{ kJ/mol}.$$

The materials (a) - (c) are familiar BMG, while (d) is a newly developed one. T_{g0} and E are the representatives of the static and kinetic terms, and no correlation can be seen between the two quantities. It is interesting to see that the E value is especially small in the case of the JA glass. Only this fact will be noted here, and more extensive studies on a variety of metallic glasses and also on other kinds of glasses are required for considering further this problem.

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FIGURE CAPTIONS

Fig. 1. DSC curves recorded for various heating rate q (K/min) for the Johnson alloy glass $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10.0}\text{Be}_{22.5}$.

Fig. 2. Observed glass transition temperature T_g (K) plotted against heating rate q (K/min), and parameter-fitted curve by Eq. (1).

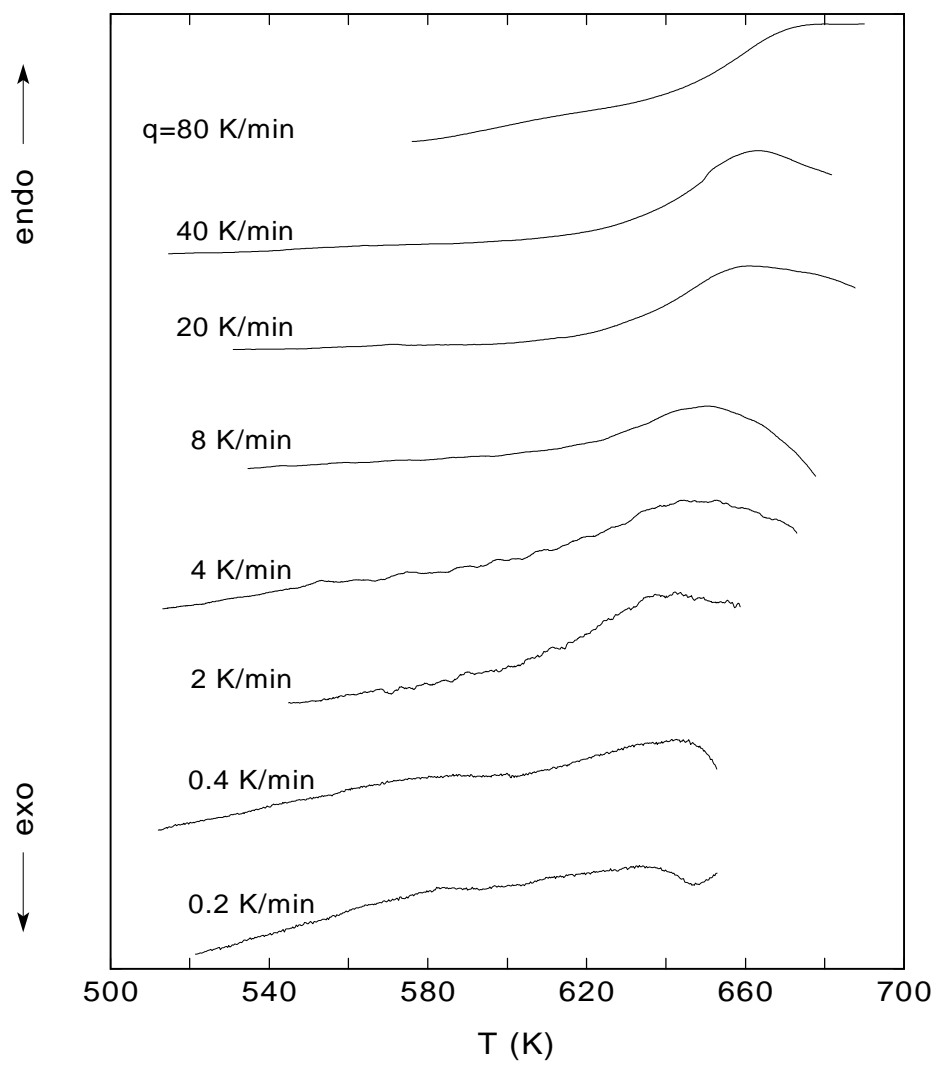


Fig. 1 Hiki and Takahashi

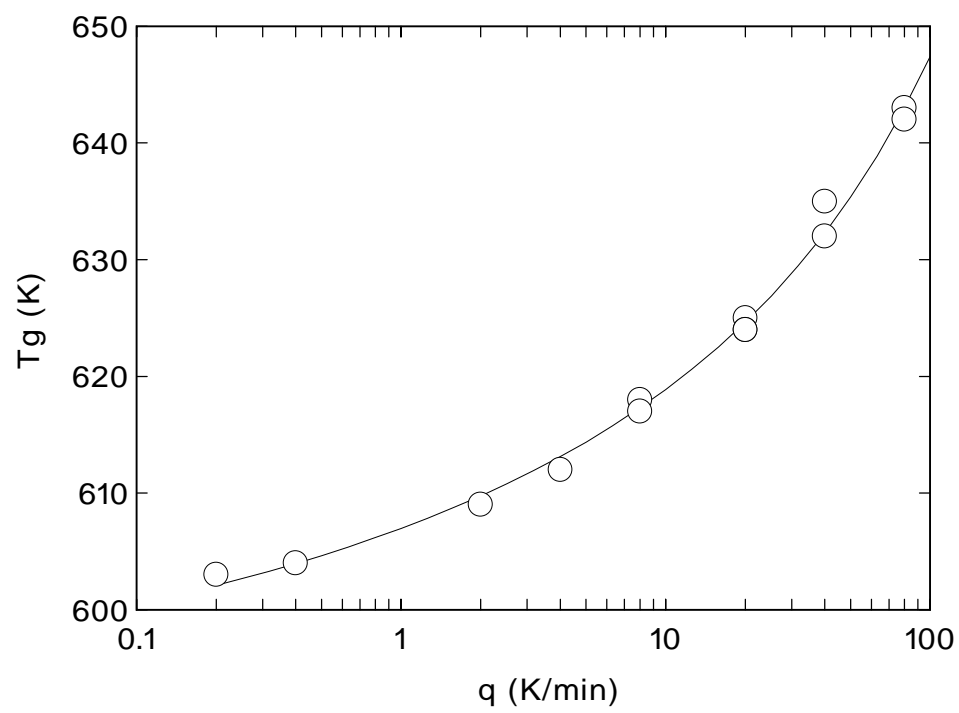


Fig. 2 Hiki and Takahashi